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(54) **Wursthüllen aus thermoplastischer Stärke und Verfahren zu deren Herstellung**

(57) Die vorliegende Erfindung betrifft die Verwendung von thermoplastisch verarbeitbarer Stärke für Wursthüllen sowie ein Extrusionsverfahren zu ihrer Herstellung.

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Abstract:

Sausage casings made of thermoplastic starch and process
for the production thereof

The present invention relates to the use for sausage casings of starch which can be processed like a thermoplastic and to an extrusion process for the production thereof.

7. The casing as claimed in claim 6, wherein it contains crosslinkers in a proportion of from 2 to 15 % by weight, preferably 5 to 10 % by weight, and/or softeners in a proportion of from 3 to 30 % by weight, preferably 5 to 20 % by weight.
8. A process for the production of sausage casings as claimed in claims 2 to 7, which comprises molding the mixture of thermoplastic starch and the remaining constituents using an extruder and a ring die attached thereto which is heated to 100 to 140°C to give a tubular casing, then inflating this and stretching it in the ratio 1:2 to 1:10, based on the surface area in each case.
9. The process as claimed in claim 8, wherein the tubular casing is stretched in the ratio of 1:3 to 1:5, based on the surface area in each case.
10. The process as claimed in claim 8 or 9, wherein an impregnation or coating is applied internally and/or externally to the stretched sausage casings.

Patent Claims

1. Use in sausage casings of starch which can be
5 processed like a thermoplastic.

2. A thermoplastic-starch-based casing for raw
 sausage, which casing, apart from thermoplastic
 starch, contains

 5 to 30 % by weight of fiber reinforcement,
10 3 to 25 % by weight of protein and
 2 to 15 % by weight of crosslinker.

3. A thermoplastic-starch-based casing for scalded-
 meat sausage and cooked ham which, apart from
 thermoplastic starch, contains 3 to 25 % by
15 weight of a fiber reinforcement.

4. The casing as claimed in claim 3, wherein it
 additionally contains synthetic polymers, cross-
 linkers and/or lubricants.

5. The casing as claimed in claim 4, wherein the
20 proportion of the synthetic polymers is 5 to 50 %
 by weight, preferably 10 to 40 % by weight, the
 proportion of the crosslinkers is 2 to 20 % by
 weight, preferably 3 to 12 % by weight and the
 proportion of the lubricants is 2 to 12 % by
25 weight, preferably 3 to 6 % by weight.

6. A thermoplastic-starch-based, fiber-free, trans-
 parent sausage casing which, in addition to
 thermoplastic starch, contains alginate,
 chitosan, extrudable cellulose derivatives and/or
30 proteins in a proportion of from 5 to 70 % by
 weight.

5.0 kg of sunflower seed oil.

The mixture was converted into a homogeneous melt using an extruder and was extruded through a ring die for caliber 80. By blow-molding in the ratio 1:6 (based on
5 the surface area), the tubular casing was then stretched longitudinally and transversely. The casing was then laid flat and rolled up. The wall thickness of the stretched casing was 95 μm . The bursting pressure of the water-soaked casing was 22 kPa. The static extension at 15 kPa
10 was 95 to 100 mm.

Casing part-pieces tied off at one end were filled with long-keeping-sausage emulsion. The sausages ripened without defect and could be easily peeled.

7.5 kg of glyoxal,
5.0 kg of triethyl acetylcitrate (^(R)Citroflex
A4) and
2.5 kg of lecithin,

5 processed in an extruder at 178°C to give a homogeneous
melt and extruded through a ring die for caliber 75. The
tubular casing was then stretched longitudinally and
transversely by blow-molding in the ratio of 1:8 (based
on the surface area), then laid flat and wound up. The
10 wall thickness of the stretched casing was 108 µm. The
bursting pressure of the water-soaked casing was 30 kPa.
The static extension at 15 kPa was 88 to 92 mm.

Sections of the tubular casing tied off at one end were
filled with "Bierwurst" emulsion. After scalding and
15 smoking, the casing could be peeled off easily from the
emulsion.

Example 4

A fiber-free casing could also be produced with starch
which had been plasticized with water instead of
20 glycerol. For this purpose,

100.0 kg of potato starch were mixed with
7.0 kg of water,
1.0 kg of sunflower seed oil and
0.5 kg of lecithin.

25 The mixture was melted in a kneader at 165°C and homoge-
nized for 1 hour. The melt was then extruded and granu-
lated.

60.0 kg of the granules thus produced were then
mixed with
30 10.0 kg of gelatin,
10.0 kg of chitosan,
10.0 kg of glycerol,
7.5 kg of glyoxal and

filled with salami emulsion and subjected to the usual ripening process. During ripening, the casing did not detach from the emulsion, i.e. "disconnection" of the casing did not occur. The peelability of the ripened salami was evaluated as "2" (rating scale of 1 to 6; 1 = very good peelability, 6 = no longer peelable).

Example 2

To produce a casing for scalded-meat\ and cooked-meat sausage and cooked ham,

10 75.0 kg of the abovedescribed granules were mixed
 with
 7.5 kg of cotton linters,
 20.0 kg of a soft, supple copolyamide,
 5.0 kg of glyoxal and
15 7.5 kg of lecithin.

The mixture was homogenized by kneading for about half an hour at 185°C and was then extruded through a ring die for caliber 60. By blow-molding, the tubular casing was then stretched longitudinally and transversely in the ratio of 1:6 (based on the surface area). The wall thickness of the stretched tube was 85 μ m. The bursting pressure of the water-soaked casings was 72 kPa, the static extension at 21 kPa was 68 mm.

25 A water-soaked casing piece tied off at one end was then filled with meat sausage emulsion. The casing could be removed without difficulty from the conventionally scalded and smoked sausage.

Example 3

To produce a fiber-free, transparent sausage casing,

30 75.0 kg of the abovedescribed granules were mixed
 with
 20.0 kg of gelatin,
 10.0 kg of chitosan

Production of the thermoplastic starch

100 kg of potato starch were dried in vacuo until the water content was less than 0.3 % by weight. The starch was then mixed with 50 kg of glycerol (99 % by weight pure) in a kneader at a temperature of 160 to 190°C. To abolish the helix structure, the melt produced in this process was kept for about 2 hours at a temperature of 170°C. It was then extruded and granulated. Even after relatively long storage, the starch remained virtually completely amorphous in the granules.

Example 1

To produce a raw sausage casing having fiber reinforcement,

75.0 kg of the abovedescribed granules (50 kg of starch + 25 kg of glycerol) were mixed with
10.0 kg of cotton linters,
10.0 kg of gelatin,
2.5 kg of adipic acid and
2.5 kg of sunflower seed oil,

extruded at 110 to 120°C and stretched longitudinally and transversely in the ratio of 1:8, based on the surface area. In this manner, a tube of caliber 60 (= 60 mm) was obtained, having a wall thickness of 90 μ m.

The tube was then laid flat, wound up and then gathered together to form concertinaed casings or finished to form sections tied off at one end.

In order to test the mechanical properties of the casing, it was soaked in water and subjected to a pressure test. It did not burst until a pressure of 65 to 72 kPa (bursting pressure) was reached. The static extension at 21 kPa was 65 to 75 mm.

In order to test the applicability, the casings were

proteins (preferably gelatin). The proportion of additional constituents is from 5 to 70 % by weight, preferably 20 to 50 % by weight. To improve the mechanical stability and the water resistance and resistance to boiling, the abovementioned crosslinkers can additionally be present in a proportion of from 2 to 15 % by weight, preferably 5 to 10 % by weight. The suppleness of the stretched sausage casing can be further improved by a softener, preferably glycerol or citric ester. The proportion of the added softener is 3 to 30 % by weight, preferably 5 to 20 % by weight.

A process for the production of starch-based sausage casings is likewise subject-matter of the present invention. The process comprises molding the mixture of thermoplastic starch and the remaining constituents using an extruder, preferably a single- or twin-screw extruder and a ring die attached thereto which is heated to 100 to 140°C, preferably 105 to 120°C to give a tubular casing, inflating this and stretching it in a ratio of 1:2 to 1:10, preferably 1:3 to 1:5, based on the surface area in each case. A homogeneous melt thus forms in the extruder. During stretching by blow molding, the casing is preferably inflated using air.

In a further step, an impregnation or coating can subsequently be applied internally and/or externally. It serves in particular to improve the sausage emulsion adhesion or to increase resistance to mold.

The starch-based sausage casings exhibit all of the positive properties of cellulose hydrate casings. The impregnations or coatings known from the cellulose hydrate casings are generally also suitable for the starch casings. In particular, layers can also be applied which act as a barrier for oxygen and/or water vapour. The starch casings can be adapted by this means to all important sausage types.

dicarboxylic acid, a dialdehyde,
a diisocyanate or a diepoxide.

These and also the following figures in % by weight
relate to the weight of the plasticized starch (total
5 weight of starch + plasticizer).

In order to satisfy the requirements for scalded-meat
sausage and cooked-meat sausage and cooked ham, fiber
reinforcement is necessary. Cotton linters, synthetic
fibers or regenerated fibers (= fibers from regenerated
10 cellulose) are particularly suitable therefor. The
proportion of fiber reinforcement is generally 3 to 25 %
by weight, preferably 5 to 15 % by weight.

A further quality improvement - depending on the appli-
cation - may be achieved by additional synthetic poly-
15 mers, preferably soft and ductile polyamides, polyesters,
polyolefins, ethylene/ethylacrylate/maleic anhydride
copolymers or polyvinylpyrrolidone (PVP). The polyolefins
are preferably low-density polyethylenes or polypropy-
lenes. The proportion of the synthetic polymers is
20 expediently 5 to 50 % by weight, preferably 10 to 40 % by
weight. Crosslinkers increase the water resistance. Their
proportion, in the casings for scalded-meat sausage and
cooked ham, is 2 to 20 % by weight, preferably 3 to 12 %
by weight. Preferred crosslinkers have already been
25 mentioned under raw sausage casings. Lubricants can
facilitate extrusion. For this purpose, the animal or
vegetable fats or lecithins already disclosed in the
abovementioned WO 90/05161 are especially suitable.
Lubricants improve the peelability and likewise the water
30 resistance. Their proportion is generally 2 to 12 % by
weight, preferably 3 to 6 % by weight.

Fiber-free, transparent casings, in addition to the
thermoplastic starch, expediently contain alginate,
chitosan, extrudable cellulose derivatives (preferably
35 cellulose acetate or cellulose propionate) and/or

optimal properties that the natural starch is converted into the amorphous state with abolition of the α -helix structure. This is successfully achieved, for example, by heating and mechanical mixing, expediently in a kneader
5 or in a single- or twin-screw extruder. In order to achieve melting of the starch below the decomposition temperature, the known plasticizers such as water, butane-1,3-diol, glycerol, diglycerol, N,N-dimethylurea, sorbitol or citrate are used.

10 When water is used as plasticizer, this is used in an amount of about 15 to 25 % by weight, preferably about 17 % by weight, based in each case on the weight of the plasticized starch. The temperature should be about 100 to 130°C. When glycerol is used as plasticizer, an amount
15 of 0.5 to 20 % by weight, preferably 8 to 16 % by weight, is sufficient, again based on the weight of the starch in each case. The temperature in this case is expediently somewhat higher. 150 to 170°C is favorable. The crystalline proportion in the thermoplastic starch should at any
20 event be less than 5 % by weight.

In order to adapt the casings to the various sausage types, suitable substances are added to the granulated thermoplastic starch. These are in particular fibers which increase the mechanical strength. Such sausage
25 casings are novel and are part of the present invention.

Casings for raw sausage, in addition to the thermoplastic starch, expediently contain

5 to 30 % by weight,	preferably 10 to 20 % by weight,
	fiber reinforcement, preferably
30	cotton combings,
3 to 25 % by weight,	preferably 5 to 15 % by weight,
	protein, preferably gelatin,
	casein or wheat protein, and
2 to 15 % by weight,	preferably 3 to 10 % by weight,
35	crosslinker, preferably a

biodegradable.

The object has been achieved by the use of starch which can be processed like a thermoplastic.

5 Natural starch, such as potato starch, corn starch or
cereal starch, is composed of macromolecules and is
highly inhomogeneous. The macromolecules occur in the
form of α -helix. On heating, the natural starch decom-
poses before it reaches the melting temperature. If water
is added in advance, a composition which can be processed
10 like a thermoplastic is obtained. Since water, because of
its low boiling point, is not so expedient in processing
terms, additives such as glycerol, ethylene glycol or
propylene glycol are more suitable, since they have a
higher boiling point. The proportion of these additives
15 should be at least 5 % by weight, based on the weight of
the dry starch.

Thermoplastic starch, process for the production thereof
and shaped bodies produced therefrom are disclosed by
WO 90/05161 and 90/10019. The applications specified
20 were: filler or formulation aid in thermoplastics and
thermosets or support material for active compounds, such
as pharmaceutical active compounds, or reagents such as
flocculents for waste water. It is stated that extruded
films of thermoplastic starch can be laid out in a low-
25 water environment or on a water-permeable underlay and
bind water. This is said to improve the efficiency of
soil irrigation in arid regions. There has been no
previous indication that thermoplastic starch could be
suitable for the production of sausage casings, espe-
30 cially those which cover a broad field of application.

The starting material used for the production of the
sausage casings is thermoplastic starch which is
disclosed in the said WO publications. This starch
generally occurs as granules or in the form of beads. It
35 is critical for the production of sausage casings having

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Sausage casings made of thermoplastic starch and process for the production thereof

- 5 The present invention relates to a tubular sausage casing and to an extrusion process for the production thereof.

In sausage production, virtually only the collagen casings (= membrane fibrous casings), the cellulose hydrate casings and casings made of synthetic polymers have achieved importance. The latter generally comprise
10 polyamide, polyethylene, polypropylene, poly(ethylene terephthalate), poly(butylene terephthalate) or poly(vinylidene chloride) copolymers. Other synthetic casings, such as casings made of protein- or acrylate-coated fabric are scarcely worthy of mention.
15

Collagen casings and cellulose hydrate casings have the advantage that they are produced from renewable raw materials, are biodegradable and thus can be composted. The processes for their production, however, are generally highly complex and environmentally polluting. Thus,
20 for example, synthetic casings based on cellulose hydrate are produced by the viscose process, in which sodium hydroxide solution and carbon disulfide are used.

The casings produced from synthetic polymers can be produced simply and inexpensively by extrusion, but they
25 are not biodegradable and must therefore be disposed of in a complex manner.

The object was therefore to provide a sausage casing which combines in itself the advantages of the known casings. It should be suitable for all sausage types, it
30 should be producible simply and in an environmentally friendly manner from renewable raw materials and be